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Thermodynamic assessments of binary phase diagrams in organic and polymeric systems

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ABSTRACT

The Sanchez–Lacombe (SL) model and the Flory–Huggins model were used for the calculation of binary phase diagrams in organic and polymer systems, respectively. The thermodynamic parameters of the liquid and gas phases in acetone–carbon disulfide (CS_2), butane–heptane, cyclohexane–aniline systems, and liquid phases in polystyrene–polybutadiene and polystyrene–bisphenol A poly-carbonate systems were optimized, based on the experimental data. The calculated results with various pressures are in good agreement with the experimental data. It is hoped that this method will be widely applied in the prediction of binary phase diagrams in organic and polymer systems.

1. Introduction

Organic and polymer materials are promising materials in many industry fields. For example, mixtures of the organic carbonates have been found to be the most suitable solvents for lithium and lithium-ion batteries because of their chemical stability against the reducing power of lithium [1]. A special class of organic molecular crystals, which is called "organic plastic crystals", is the potential thermal energy storage materials that undergo solid–solid phase transitions storing a significant amount of thermal energy, and can be incorporated in practical applications such as drywall and Trombe walls in passive solar buildings [2]. Spinodal decomposition is ubiquitous for polymer systems, and may be used to manufacture products with predefined mechanical, thermal, chemical and/or electrical properties. A number of functional polymeric materials were fabricated by spinodal decomposition [3]. To understand phase relations in polymeric solutions, thermodynamic theories and models have been proposed, including the Sanchez–Lacombe (SL) model [4], the Flory–Huggins model [5], and the Universal quasi-chemical activity coefficient (UNIQUAC) model [6,7].

Phase diagram is a powerful tool for designing materials. For example, the liquid–vapor phase diagrams in organic systems are widely applied in purification, while the phase diagram with liquid phase separation of polymer system is used for the constitution design of materials. CALPHAD (Calculation of Phase Diagrams) method is an important tool for designing new materials because it can significantly decrease cost and time during development of materials and provide clear guidelines for material design [8–10], and is widely used in inorganic systems. However, little work has been carried out on the calculation of phase diagrams in organic and polymer systems.

The purpose of the present paper is (1) to propose the calculated methods of binary phase diagrams of both organic and polymer systems, and (2) to carry out thermodynamic assessments of some binary phase diagrams in organic and polymer systems by combining the SL model and the Flory–Huggins model with the experimental data.

2. Thermodynamic models

2.1. SL model for organic systems

The SL model was proposed by Sanchez and Lacombe [4,11,12] based on an Ising fluid theory. The reduced Gibbs free energy $\widetilde{G}$ of the SL model is given, as follows:

$$\widetilde{G} = -\widetilde{\rho} + \widetilde{P}\widetilde{v} + \widetilde{T}\left[(\widetilde{v}-1)\ln(1-\widetilde{\rho}) + \frac{1}{r}\ln\widetilde{\rho} + \frac{\varphi_1}{r_1^0}\ln\varphi_1 + \frac{\varphi_2}{r_2^0}\ln\varphi_2\right], \quad (1)$$

where $\widetilde{T}$, $\widetilde{P}$, $\widetilde{v}$, and $\widetilde{\rho}$ are the reduced temperature, pressure, volume, and density, respectively, and expressed as:

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$$\widetilde{T} \equiv T/T^*, \qquad T^* \equiv \varepsilon^*/k,$$
$$\widetilde{P} \equiv P/P^*, \qquad P^* \equiv \varepsilon^*/v^*,$$
$$\widetilde{v} \equiv \frac{1}{\widetilde{\rho}} \equiv V/V^* \equiv \frac{1}{f}, \qquad V^* = N(rv^*),$$
$$\frac{1}{r} = \frac{\varphi_1}{r_1^0} + \frac{\varphi_2}{r_2^0},$$
$$v^* = \frac{\varphi_1}{\varphi_1 + \frac{v_1^*}{v_2^*}\varphi_2} v_1^* + \frac{\frac{v_1^*}{v_2^*}\varphi_2}{\varphi_1 + \frac{v_1^*}{v_2^*}\varphi_2} v_2^*,$$
$$\varepsilon^* = \sum\sum \varphi_i\varphi_j\varepsilon_{ij}^* = \sum \varphi_i\varepsilon_{ii}^* - \sum\sum \varphi_i\varphi_j\xi_{ij},$$
$$\xi_{ij} = \varepsilon_{ii}^* + \varepsilon_{jj}^* - 2\varepsilon_{ij}^*.$$

where v_i^*, r_i^0 and ε_{ii}^* are molecular parameters to characterize a pure fluid, and ξ_{12} is the parameter that characterizes a binary mixture. φ_i represents the composition of component i, and can be expressed as a function of moles of components n_i : $\varphi_i = \frac{n_i}{\sum n_i}$.

In this paper, the parameter of ξ_{12} is expressed as a function of temperature and composition, as in the CALPHAD method, given by

$$\xi_{12} = \sum_{k=0}^{n} (A_k + B_k)(\varphi_1 - \varphi_2)^k, \tag{2}$$

where A_k and B_k are model parameters, to be evaluated on the basis of the experimental data.

The value of the reduced density $\widetilde{\rho}$ is derived in the usual way,

$$\left.\frac{\partial \widetilde{G}}{\partial \widetilde{v}}\right|_{\widetilde{T},\widetilde{P}} = 0, \tag{3}$$

which yields the equation of state,

$$\widetilde{\rho}^2 + \widetilde{P} + \widetilde{T}\left[\ln(1-\widetilde{\rho}) + \left(1 - \frac{1}{r}\right)\right]\widetilde{\rho} = 0. \tag{4}$$

2.2. Flory–Huggins model for polymer systems

The Flory–Huggins model is widely used in polymer phase diagram calculation [5,13]. The Gibbs free energy G can be described as follows:

$$\frac{\Delta G}{RT} = \frac{\rho_1}{M_1}\varphi_1 \ln\varphi_1 + \frac{\rho_2}{M_2}\varphi_2 \ln\varphi_2 + \chi_{12}\varphi_1\varphi_2, \tag{5}$$

where M_i is the molecular weight of component i, and φ_i the volume fraction which can be expressed as a function of molar volume V_i and moles N_i of component i: $\varphi_i = \frac{N_iV_i}{\sum N_iV_i}$.

ρ_i represents the density of polymer segment, and is estimated from the monomer weight and volume of the polymer. The monomer volume of the polymer can be roughly estimated from the group-contribution scheme of Bondi [14].

The first two terms in Eq. (5) are the Flory–Huggins configurational chain entropies. The third term is the excess free energy, and χ_{12} is the interaction parameter of components 1 and 2.

In the present paper, χ_{12} is represented as a function of temperature and composition of component, in the following form:

$$\chi_{12} = \sum_{k=0}^{n} (A_k + B_kT)(\varphi_1 - \varphi_2)^k, \tag{6}$$

where A_k and B_k are coefficients to be evaluated from the experimental data.

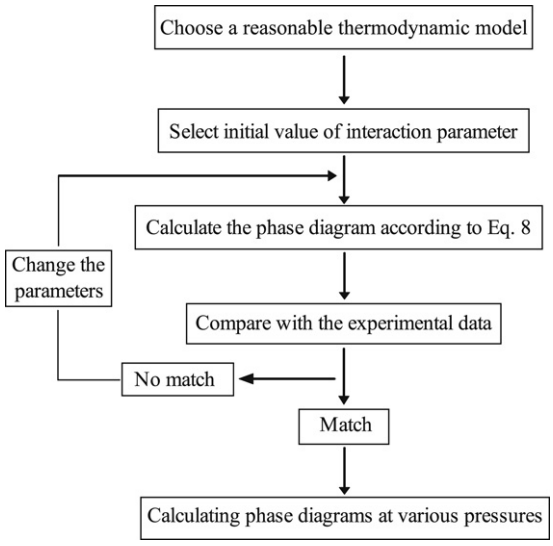


Fig. 1. The flow chart of the program for estimating model parameters and calculating phase diagrams.

2.3. Calculation method

According to the principle of phase diagram calculation, the α/β phase equilibrium in a binary mixture is determined by the following conditions on the chemical potentials:

$$\mu_1^\alpha = \mu_1^\beta, \qquad \mu_2^\alpha = \mu_2^\beta. \tag{7}$$

These equations can be expressed by:

$$\frac{\partial G^\alpha}{\partial \varphi} = \frac{\partial G^\beta}{\partial \varphi} = \frac{\Delta G}{\Delta \varphi}. \tag{8}$$

Phase diagrams can be calculated using Eq. (8) by our own computer program, which was compiled by Matlab and Maple. Trial-and-error method was used to estimate the model parameters. The flow chart of the program for calculating phase diagram is given in Fig. 1.

3. Experimental information

3.1. Organic systems

The liquid–vapor phase diagram of acetone–carbon disulfide (CS_2) at $P = 1$ atm was measured by Rosanoff and Easley [15], where the liquid/vapor equilibrium was established with reference both to temperature and to partial and total vapor pressures, and the analyses of the liquid mixtures were carried out by the refractometric method at desired temperatures. All these data were compiled by Chu et al. [16].

The liquid–vapor phase diagram in butane–heptane system at $P = 6.8$ atm was determined by Kay, and the phase diagram in the cyclohexane–aniline system at $P = 1$ atm was measured by Timmermans. All these data were compiled by Jean Timmermans [17].

3.2. Polymer systems

Phase equilibria in the polybutadiene–polystyrene (PBD–PS) system with various molecular weights were investigated by Roe and Zin [18] using a laser light scattering method. The temperature on heating was taken as the cloud point, and it was usually higher by a few degrees (up to 8 °C in some cases) than the temperature

Table 1
Parameters of organic compounds [4].

Organic compounds	Formula	r^0	v^* (cm^3 mol^{-1})	ε^* (J mol^{-1})
Acetone	CH_3COCH_3	8.4	7.54	4036
Carbon disulfide	CS_2	5.95	9.15	4729
Butane	$CH_3CH_2CH_2CH_3$	7.59	10.4	3368
Heptane	$CH_3(CH_2)_5CH_3$	9.57	13.09	4061
Cyclohexane	C_6H_{12}	8.65	10.79	4145
Aniline	$C_6H_5NH_2$	10.3	8.11	5124

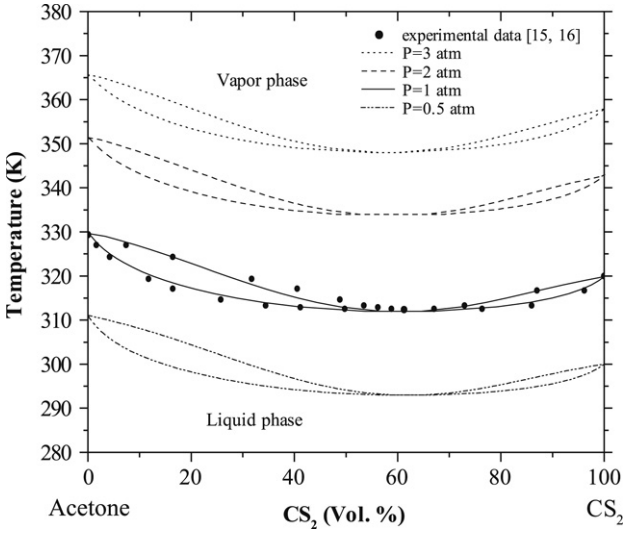


Fig. 2. Calculated liquid–vapor phase diagram in acetone–carbon disulfide (CS_2) system compared with the experimental data [15,16].

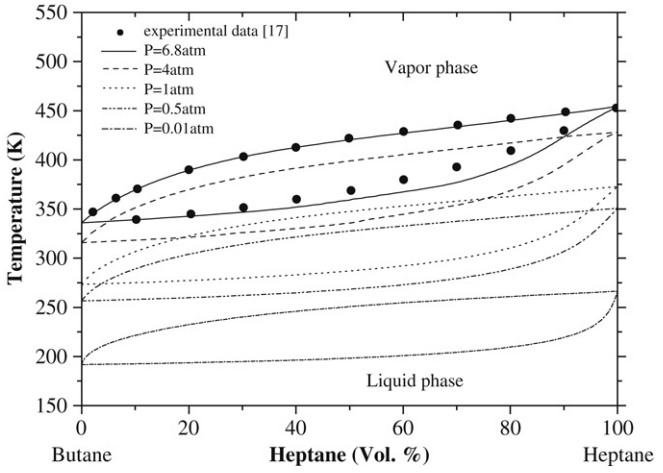


Fig. 3. Calculated liquid–vapor phase diagram in butane–heptane system compared with the experimental data [17].

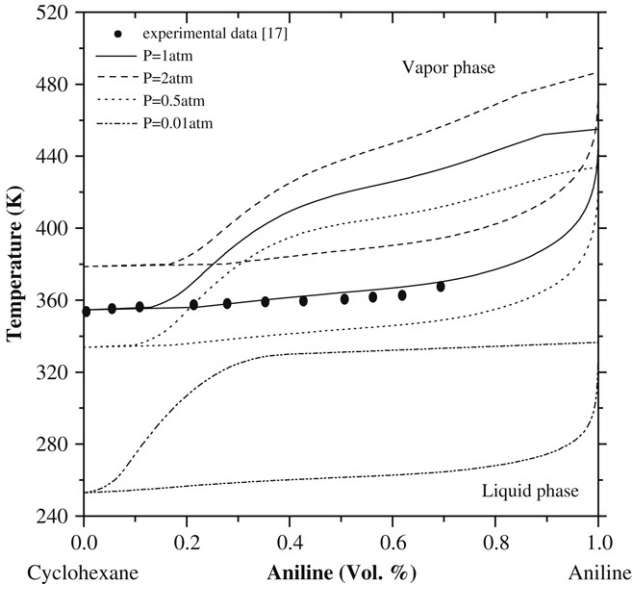


Fig. 4. Calculated liquid–vapor phase diagram in cyclohexane–aniline system compared with the experimental data [17].

at which the turbidity first appeared on cooling. All measurements were performed at 2 °C/min.

The phase diagram in the polystyrene–tetramethylbisphenol A polycarbonate (PS–TMBPA-PC) system was investigated by Casper, and Morbitzer [19], using differential scanning calorimetry (DSC) at 16 °C/min. The measured samples were cast to be films with the thickness of 50–100 nm, and then dried at 70 °C in the vacuum for 48 h and annealed at 230 °C for 1 h. The molecular weights of polystyrene and tetramethylbisphenol A polycarbonate were 3×10^5 and 4×10^4, respectively.

4. Results and discussion

4.1. Organic systems

According to the experimental data [15–17], the parameters (ξ_{12}) of acetone–carbon disulfide (CS_2), butane–heptane and cyclohexane–aniline systems were evaluated. The molecular parameters (v_i^*, r_i^0 and ε_{ii}^*) of each organic compound are shown in Table 1, and the evaluated parameters (ξ_{12}) with the temperature T and compositions φ_i dependences are presented in Table 3. The calculated phase diagrams of organic systems are shown in Figs. 2–4.

Fig. 2 shows the calculated liquid–vapor phase diagram of acetone–carbon disulfide (CS_2) compared with the experimental data [16]. It is seen from Fig. 2 that there is a minimum in the boiling point curve and a lower azeotrope in acetone/carbon disulfide system. The calculated azeotropic composition is 0.62 at 312 K, in excellent agreement with the experimental data of 0.66 at 312.2 K. The phase diagrams at $P = 0.01$, 0.5, 2, and 3 atm are also predicted using the evaluated parameters.

The calculated liquid–vapor phase diagram of butane–heptane is shown in Fig. 3. The calculated vapor curve is in reasonable agreement with the experimental data [17]. However, there are some deviations on the liquidus between the calculated results and the experimental data. The deviations may be due to the errors of the experiments or the calculation, which are acceptable in all. Using the evaluated parameters, the phase diagrams at $P = 0.5$, 1 and 4 atm are predicted. The calculated liquid–vapor phase diagram in the cyclohexane–aniline system is shown in Fig. 4, where the calculated results with various pressures ($P = 0.01$, 0.5,

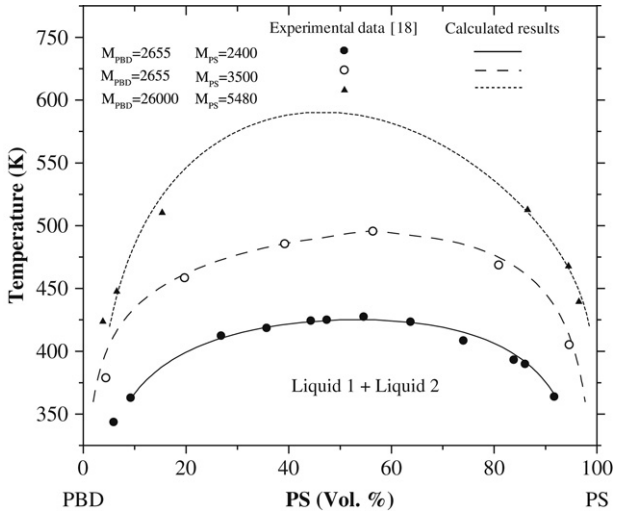


Fig. 5. Calculated phase diagrams in polybutadiene (PBD)–polystyrene (PS) system compared with the experimental data [18].

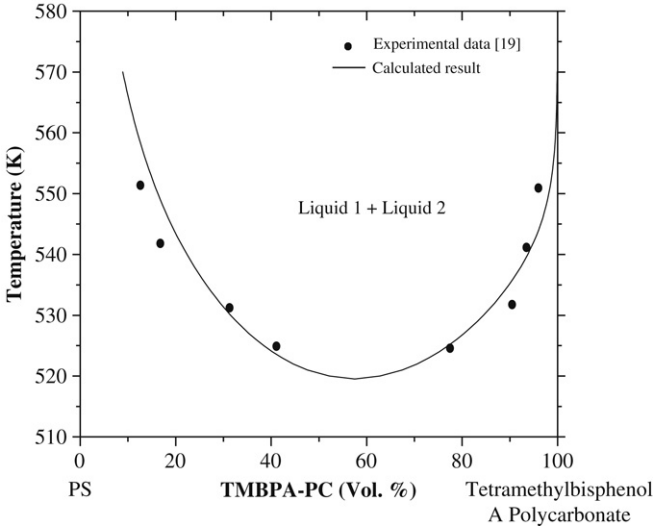


Fig. 6. Calculated phase diagram in polystyrene (PS)–tetramethylbisphenol A polycarbonate (TMBPA-PC) system compared with the experimental data [19].

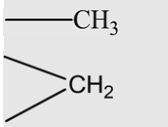
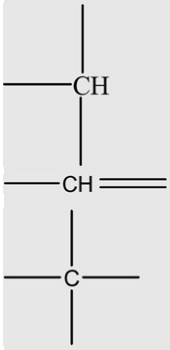
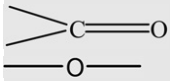
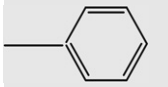
2, and 3 atm) are also presented, showing good agreement with available experimental data.

Liquid-vapor phase diagrams of organic systems at various pressures are widely used for material engineering. In particular, the phase diagrams at reduced pressures are expected for the process of purifying. Therefore, phase diagrams at various pressures are also predicted. The calculated results indicate that the liquidus and vaporus shift to higher-temperature and the liquid vapor two-phase region becomes narrow with the increasing of pressure.

4.2. Polymer system

The group contributions to the Van der Waals volume [14] of each polymer segment are presented in Table 2. Using these data, the polymer–polymer interaction parameters (χ_{12}) in the liquid phase were evaluated in polybutadiene–polystyrene and polystyrene–tetramethylbisphenol A polycarbonate (TMBPA–PC) systems, and are presented in Table 3. The calculated phase diagrams are shown in Figs. 5 and 6. Furthermore, the calculated

Table 2
Group contributions to the Van der Waals volume [14].

Groups	The Van der Waals volume V_w ($cm^3\ mol^{-1}$)
	13.67
	10.23
	6.78
	8.47
	3.33
	11.7
	3.2
	45.84

critical temperature T_c for each system, which is useful in material design, is also shown in Table 4.

Fig. 5 shows the liquid–liquid phase diagrams of polymer systems of different molecular weights. The polybutadiene–polystyrene system shows an upper critical solution temperature (UCST) in Fig. 5. The calculated results are in good agreement with experimental data [18]. However, there are some errors in the system with $M_{PBD} = 26\,000$, $M_{PS} = 5480$, due to a lack of the experimental critical data.

In Fig. 6, the phase diagram in the polystyrene–tetramethylbis phenol A polycarbonate system exhibits a lower critical solution temperature (LCST). The calculated results are also in good agreement with experimental data [19]. This demonstrates that the present model can describe the features of polymer phase diagrams.

5. Conclusions

(1) The methods for calculating the phase diagrams in both organic and polymer systems were proposed. The Sanchez–Lacombe (SL) model and the Flory–Huggins model were used for the calculation of binary phase diagrams of organic and polymer systems, respectively.

(2) The thermodynamic parameters in five binary systems were evaluated, based on the available experimental data in the literature. Good agreement between the calculated results and most of the experimental data was obtained.

(3) According to these parameters, the binary phase diagrams at various pressures of organic systems are also predicted.

Acknowledgments

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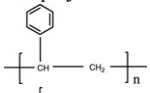
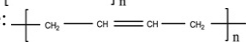
Table 3
Thermodynamic parameters of organic and polymer systems.

Systems	Parameters
Acetone–CS_2	$\xi_{12} = 951 - 0.315T + (-114 + 0.096T)(\varphi_A - \varphi_B) + (17 + 0.018T)(\varphi_A - \varphi_B)^2$
Butane–Heptane	$\xi_{12} = 639 - 0.176T + (-48 + 0.203T)(\varphi_A - \varphi_B) + (18 - 0.028T)(\varphi_A - \varphi_B)^2$
Cyclohexane–Aniline	$\xi_{12} = -2331 + 8.964T + (184 + 0.230T)(\varphi_A - \varphi_B) + (1037 - 0.346T)(\varphi_A - \varphi_B)^2$
Polybutadiene-Polystyrene	
$M_{PBD} = 2655, M_{PS} = 2400$	$\chi_{12} = 0.0043 - 7.1 * 10^{-6}T + (0.0003 - 6.9 * 10^{-7}T)(\varphi_A - \varphi_B) + (0.000324 - 6.4 * 10^{-7}T)(\varphi_A - \varphi_B)^2$
$M_{PBD} = 2655, M_{PS} = 3500$	$\chi_{12} = 0.00454 - 7.18 * 10^{-6}T + (0.00021 - 6.9 * 10^{-7}T)(\varphi_A - \varphi_B) + (0.000324 - 6.4 * 10^{-7}T)(\varphi_A - \varphi_B)^2$
$M_{PBD} = 26\,000, M_{PS} = 5480$	$\chi_{12} = 0.001595 - 2.22 * 10^{-6}T + (0.00019 - 1.2 * 10^{-7}T)(\varphi_A - \varphi_B) + (0.00004 - 5 * 10^{-8}T)(\varphi_A - \varphi_B)^2$
Polystyrene–Tetramethylbisphenol A polycarbonate	
$M_{PS} = 300\,000, M_{PC} = 40\,000$	$\chi_{12} = -0.0004655 + 9.63 * 10^{-7}T + (-8.5 * 10^{-6} + 2 * 10^{-8}T)(\varphi_A - \varphi_B) + (-0.00003 + 3.8 * 10^{-8}T)(\varphi_A - \varphi_B)^2$

Note: Formula of polymers:

Polystyrene: 

Polybutadiene: 

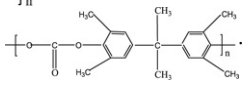
Tetramethylbisphenol A polycarbonate:  .

Table 4
Comparison of the critical temperatures and composition between the calculated results and the experimental data.

Systems	Calculated critical temperature (K)	Calculated critical composition	Experimental critical temperature (K)	Experimental critical composition
Polybutadiene–Polystyrene				
$M_{PBD} = 2655, M_{PS} = 2400$	426	0.535	427.6 [18]	0.546 [18]
$M_{PBD} = 2655, M_{PS} = 3500$	495	0.583	495.6 [18]	0.564 [18]
$M_{PBD} = 26000, M_{PS} = 5480$	591	0.465	–	–
Polystyrene-tetramethylisphenol A polycarbonate				
$M_{PS} = 300\,000, M_{PC} = 40\,000$	519.5	0.5752	–	–

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